

Determination of the activation parameters $[\Delta H^\ddagger]$ and $[\Delta S^\ddagger]$ via a kinetic study of substituted secondary alcohols oxidation by using polymer supported chromic acid in the presence of 1,4 dioxane as a promoter

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Abstract

Chromic acid oxidation of substituted secondary alcohols in the presence of 1,4 dioxane has been studied by the rate of disappearance of Cr(VI). The reaction is zero order with respect to [Cr(VI)]. The reagent supported on anion exchange resin was found to be more efficient in the oxidation reaction. The reagent is very easily separated from the reaction mixture and can be manually removed from the reaction mixture, which remains clear during and after the reaction. For the study kinetics of oxidation of aromatic secondary alcohols 4-Bromophenylethanol, 4-Chlorophenylethanol and 4-Iodophenylethanol with chromic acid supported on anion exchange resins like Amberlite 400 [Cl⁻] in 1,4-dioxane has been studied. The reaction is found to be of zero order dependence of alcohol and oxidant. The activation parameters like $[\Delta H^\ddagger]$ and $[\Delta S^\ddagger]$ with respect to the first step of the suggested mechanism were evaluated and discussed.

Keywords Chromium (VI), Activation parameters, secondary alcohols, 1,4-dioxane

1. Introduction

Chromium (VI) acts as a powerful oxidizing agent in different types of redox reactions and is converted into chromium (III). Different mechanistic routes have been suggested for the reduction of chromium (VI) to chromium (III) from analysis of kinetic data and other experimental findings. The mode of reduction largely depends on the nature of the reductant and the experimental conditions.¹⁻⁴ Intermediates like Cr (V) and Cr (IV) have been identified and characterized in many cases. To explore all these aspects Cr (VI) has been extensively studied in redox kinetics. Here, it is

important to note that, Cr (VI) is hazardous because of its carcinogenic and mutagenicity.⁵⁻⁸ This is why studies on the kinetics and mechanism of Cr(VI) oxidation of biologically relevant reducing agents are of interest to both biochemists and inorganic chemists.¹⁻³ During the reduction of Cr(VI) to Cr(III), the intermediate oxidation states of chromium may interact with biologically active molecules and induce toxicity.³ Thus, in terms of chromate toxicity, it is reasonable to assume that the reducing agent may have an important role. The present research paper deals with three-electron (3e⁻) transfer Cr(VI) oxidation of aromatic secondary alcohols in the presence of 1,4 dioxane as a promoter. It was reported by Dominic and Rocek^{9,10} that unanalyzed chromic acid oxidation of substituted secondary alcohols proceeds via three-electron transfer as the rate-determining step and involves simultaneous rupture of 'C-C' and 'C-H' bonds within a cyclic transition state.

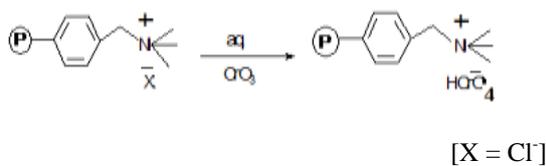
The State of California has set a limit on the average concentration of hydrocarbons at 275 ppm as hexane equivalent emitted from such a catalytic device during a test cycle. Likewise an average of 1.5% carbon monoxide is allowable in the exhaust effluent from Chromium compounds have been used in aqueous and non-aqueous medium for oxidation of variety of organic compounds. Chromium compounds especially chromium(VI) reagent are capable of oxidizing almost all the oxidative organic functional groups. The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to be chromium containing compounds like tri/tetra alkyl ammonium halo chromates have been used as oxidant for the oxidation of various organic substrates.¹⁰⁻¹²

2. Material and method

Reagent grade chemicals and doubly distilled water were used throughout the work. All other reagents used were of analytical grade and their solutions were prepared by dissolving requisite amount of the sample in doubly distilled water.

Preparation of supported oxidizing agent

The supported oxidizing agent was prepared by reported method¹³⁻¹⁵. The chloride form of Amberlite 400[Cl⁻] [a macro reticular anion exchange resin] congaing a quaternary ammonium group was stirred with a saturated solution of chromium trioxide in water for 20 min at room temperature using a magnetic stirrer. The chloride ion was readily displaced and HCrO₄⁻ form of resin was obtained in 50 min. The resin was successively rinsed with water, acetone and THF and finally dried in vacuum at 323 K for 2 hrs. The dried form of the resin was stored and used throughout the kinetic study.



Determination of the capacity of chromate form of the polymeric reagent

The capacity of the chromate form of Amberlite 400 [Cl⁻] polymeric reagent was determined by iodometrically. The capacity of the chromate form of resin was 1.75eq/L and used throughout work. The loading was also determined by elemental nitrogen analysis and was found to be 3.215 eq/L.¹⁶⁻¹⁷

Test for acrylonitrile polymerization

Under the experimental conditions, polymerization of acrylonitrile occurred under a nitrogen atmosphere. This indicates the generation of free radicals during the reaction¹⁸⁻²⁰.

Kinetic Measurements

The reaction mixture for the kinetic run was prepared by mixing aromatic secondary alcohol, oxidant and solvent. The reaction was carried out either constant stirring using magnetic stirrer and at a constant temperature 318 K. At different time interval, the reaction mixture was withdrawn using a micropipette. The aliquot thus withdrawn was taken in a stopper test tube containing 5 x 10⁻³ dm³ of 1,4-dioxane and subjected to spectral analysis. The absorbance of the product formed was measured

using Schmadzu 1800 UV-visible spectrophotometer kinetic study.

Table 1 Product analysis

Melting point of 2,4DNPhydrazone Derivative	K	Yield in %	UV λ max	Lit. UV λ max
4-Bromoacetophenone	237	98	242	245
4-Chloroacetophenone	245	97	259	263
4-Iodoacetophenone	274	96	278	276

Evaluation of the activation parameters

From the studies of the effect of temperature on the rate constant (k), the activation parameters, ΔH[#](enthalpy of activation) and ΔS[#](entropy of activation) have been evaluated by using the Eyring equation

$$\ln(kh/k_nT) = \Delta H^\# / RT - \Delta S^\# / R$$

Where k_n is the Boltzman constant (1.38 x 10⁻²³ JK⁻¹), h is Planks constant (6.62x 10⁻³⁴ Js⁻¹) and R is the molar gas constant (8.31JK⁻¹mol⁻¹). Free energy of activation (ΔG[#]) and its errors can also be calculated from the following equations.

$$\Delta G^\# = RT \ln(kn/hk)$$

and

$$\partial \Delta G^\# = RT (\partial k / k)$$

Table 2. Activation Parameters

Activation Parameters	[ΔH [#]] kJ mol ⁻³	[ΔS [#]] kJ mol ⁻³
4-Bromoacetophenone	54	-71
4-Chloroacetophenone	76	-82
4-Iodoacetophenone	78	-94

3. Results and Discussion

Influence of varying temperature

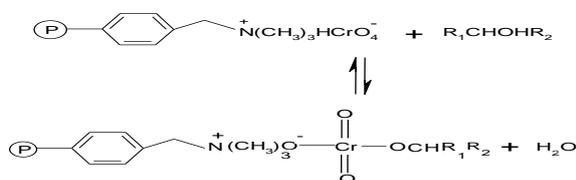
The reaction was carried out at four different temperatures under otherwise similar reaction condition to study the effect of temperatures on the rate of reaction. It was observed that, the rate of reaction increased with an increase in temperature.[Table-4].The activation parameters like energy of activation[Ea].enthalpy of activation [ΔH[#]]

, entropy of activation $[\Delta S^\ddagger]$ free energy of activation $[\Delta G^\ddagger]$ the high positive value of free energy of activation state is highly solved and frequency factor $[A]$ were calculated by determining value of K at different temperature [Table-5] on the bases of above experimental results the following reaction scheme is proposed for Cr(VI) catalyzed oxidation of various aromatic secondary alcohols. The mechanism is suggested in scheme (I) and involves ester formation.^{12,13}

Table 3. Influence of varying weights of oxidant on reaction rate at 318K.

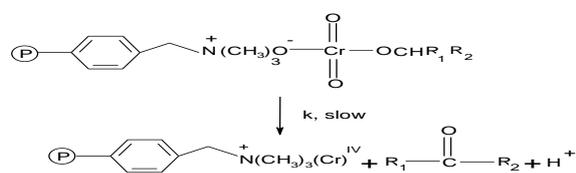
Rate constant	$\rightarrow k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Oxidant $\times 10^{-6} \text{ Kg}$	100	120	140	160
4-Bromoacetophenone	1.25	1.24	1.25	1.29
4-Chloroacetophenone	1.52	1.55	1.85	1.87
4-Iodoacetophenone	1.98	2.05	2.10	2.12

1) The polymer supported reagent reacts with a molecule of alcohol to form a chromate ester. (Step-1)



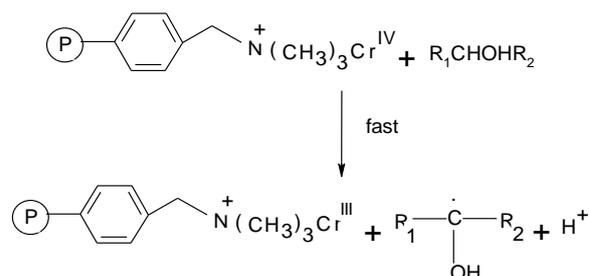
Step-1

2) The ester formed will decompose into ketone and the intermediate chromium (VI) will be formed in the second step. (Step-2)



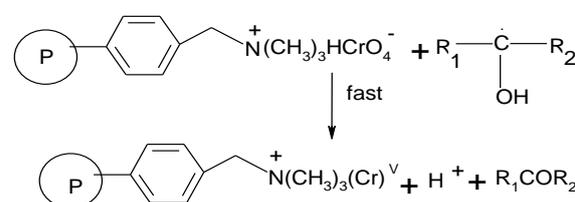
Step-2

3) The intermediate chromium (VI) thus reacts with another alcohol molecule to produce a free radical species. The free radical species formation in the reaction was confirmed by the polymerization of added acrylonitrile or addition of acidified methanol into the mixture. (Step-3)



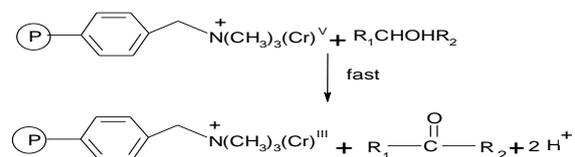
Step-3

4) Subsequently the free radical will react with another site in the polymeric reagent in a fast step leading to the formation of chromium(V). (Step-4)



Step-4

5) The intermediate chromium (V) in the last step reacts with 1-phenylethanol produce acetophenone. The test for formation of chromium (V) and (IV) by the characteristic induced oxidation of iodide and manganese (II) were not probably due to heterogeneity of the reaction mixture. (Step-5)



[$\text{R}_1 = \text{CH}_3-\text{C}_6\text{H}_4-$ and $\text{R}_2 = -\text{CH}_3$]

Step-5

4. Product analysis and stoichiometry

Product analysis was carried out by using the 2,4-dinitrophenylhydrazine (DNP) test. The solution of the reaction product was treated with an excess of a saturated solution of DNP in dilute hydrochloric acid. The precipitated 2,4-dinitrophenylhydrazone was filtered off, dried and recrystallized from ethanol. The melting point of the DNP derivative (230 °C) was found to be lower than the melting point (239 °C) of the DNP derivative of authentic substituted ketone. This slight lowering of the melting point was due to the presence of the DNP derivative of substituted ketone produced as a by-product in a small amount.

5. Conclusion

ΔH^\ddagger , indicates that the path is favored mainly due to very high negative value of the entropy of activation, ΔS^\ddagger . The negative value of ΔS^\ddagger and composite rate constant *kcal* support the suggested cyclic transition state.¹⁶⁻²⁴

Acknowledgements

I acknowledge the department of chemistry of B.Raghunath Arts, Commerce and Science College, Parbhani, Maharashtra gratefully appreciated.

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